

(19) World Intellectual Property Organization  
International Bureau



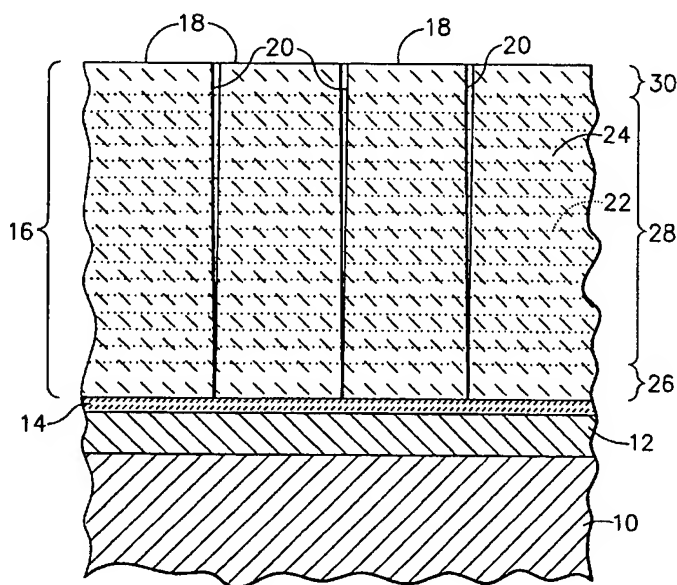
(43) International Publication Date  
30 August 2001 (30.08.2001)

PCT

(10) International Publication Number  
**WO 01/63008 A2**

- (51) International Patent Classification<sup>7</sup>: **C23C 28/00** (74) Agents: **CRISS, Roger, H.** et al.; Honeywell International Inc., 101 Columbia Avenue, P.O. Box 2245, Morristown, NJ 07962-2245 (US).
- (21) International Application Number: **PCT/US01/09266**
- (22) International Filing Date: **22 March 2001 (22.03.2001)** (81) Designated State (national): **JP.**
- (25) Filing Language: **English** (84) Designated States (regional): **European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR).**
- (26) Publication Language: **English**
- (30) Priority Data:  
09/535,394 24 March 2000 (24.03.2000) **US**  
Published:  
— upon request of the applicant, before the expiration of the time limit referred to in Article 21(2)(a)  
— without international search report and to be republished upon receipt of that report  
— without classification; title and abstract not checked by the International Searching Authority
- (71) Applicant: **HONEYWELL INTERNATIONAL INC.**  
[US/US]; 101 Columbia Avenue, P.O. Box 2245, Morristown, NJ 07960 (US).
- (72) Inventors: **STRANGMAN, Thomas, E.**; 7632 North 22nd Street, Phoenix, AZ 85020 (US). **RAYBOULD, Derek**; 2 Horizon Drive, Denville, NJ 07834 (US).  
For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: **LOWER CONDUCTIVITY THERMAL BARRIER COATING**



(57) Abstract: A thermal barrier coating for superalloy articles such as turbine engine vanes and blades that are exposed to high temperature gas is disclosed. The coating includes a columnar grained ceramic layer applied to an aluminide or MCrAlY bond coat by electron beam physical vapor deposition. The ceramic layer is comprised a plurality of layers of zirconia stabilized with 20 percent yttria and the interfaces between the layers are decorated with particles selected from a group consisting of Ta<sub>2</sub>O<sub>5</sub> and alumina. Though not essential to the invention a layer of tetragonal zirconia may be deposited both under and over the ceramic coat. An improved electron physical beam vapor deposition process for applying this ceramic layer is also disclosed.

WO 01/63008 A2

# 1 LOWER CONDUCTIVITY THERMAL BARRIER COATING

## TECHNICAL FIELD

5           This invention relates generally to thermal barrier coatings for superalloy substrates and in particular to a multilayer, ceramic thermal barrier coating having low thermal conductivity for superalloy blades and vanes in gas turbine engines.

## BACKGROUND OF THE INVENTION

10           As gas turbine engine technology advances and engines are required to be more efficient, gas temperatures within the engines continue to rise. However, the ability to operate at these increasing temperatures is limited by the ability of the superalloy turbine blades and vanes to maintain their mechanical strength when exposed to the heat,  
15           oxidation, and corrosive effects of the impinging gas. One approach to this problem has been to apply a protective thermal barrier coating which insulates the blades and vanes and inhibits oxidation and hot gas corrosion.

            Typically, thermal barrier coatings are applied to a superalloy  
20           substrate and include a bond coat and a ceramic top layer. The ceramic top layer is applied either by the process of plasma spraying or by the process of electron beam physical vapor deposition (EB-PVD). Use of the EB-PVD process results in the outer ceramic layer having a columnar grained microstructure. Gaps between the individual columns allow the

columnar grains to expand and contract without developing stresses that could cause spalling. Strangman, U.S. Pat. Nos. 4,321,311, 4,401,697, and 4,405,659 disclose thermal barrier coatings for superalloy substrates that contain a MCrAlY layer, an alumina layer, and an outer columnar  
5 grained ceramic layer. A more cost effective system is disclosed in Strangman U.S. Patent No. 5,514,482 which teaches a thermal barrier coating for a superalloy substrate that contains an aluminide layer, an alumina layer, and an outer columnar grained ceramic layer.

The ceramic layer is commonly zirconia stabilized with yttria. The  
10 prior art teaches that the amount of yttria can range from 6 percent to 35 percent of the layer. (see U.S. Patent Nos. 5,238,752 and 4,321,310). It is also known in the prior art that cubic zirconia, which is zirconia stabilized with 20 percent yttria, has a significantly lower thermal conductivity relative to tetragonal zirconia which is stabilized with 6 to 8 percent yttria.  
15 However, despite the disadvantage of higher thermal conductivity most commercially available thermal barrier coatings use tetragonal zirconia stabilized with 7 percent yttria for the ceramic layer because it is more reliable due to its superior capability to resist spalling and particulate erosion.

20 Accordingly, there is a need for a thermal barrier coating having a ceramic layer that has thermal conductivity less than or equal to that of

cubic zirconia and resistance to spalling of tetragonal zirconia as well as a need for a method to make such a coating.

### SUMMARY OF THE INVENTION

An object of the present invention is to provide a superalloy article  
5 having a ceramic layer that has thermal conductivity less than or equal to that of cubic zirconia and resistance to spalling of tetragonal zirconia.

Another object of the present invention is to provide a thermal barrier coating system having a ceramic layer that has thermal conductivity less than or equal to that of cubic zirconia and resistance to  
10 spalling of the tetragonal zirconia.

Yet another object of the present invention is to provide an improved electron beam - physical vapor deposition process for making such ceramic layers.

Yet still another object of the present invention is to provide a  
15 chamber for use in such improved electron beam - physical vapor deposition process.

The present invention achieves these objects by providing a thermal barrier coating that includes an aluminide or MCrAlY bond coat and a columnar ceramic layer applied to the bond coat by electron beam -  
20 physical vapor deposition. The ceramic coat is comprised of a plurality of

layers of cubic zirconia stabilized with 20 percent yttria with the interfaces<sup>4</sup>  
between layers decorated with particles selected from a group of second  
phase metal oxides such as  $Ta_2O_5$  and alumina. The preferred  
concentration of  $Ta_2O_5$  and/or alumina particles within the yttria stabilized  
5 zirconia is 1 to 4 weight %. An alternative is to codeposit the second  
phase metal oxide with the stabilized zirconia. Though not essential to the  
invention a layer of tetragonal zirconia stabilized with 7% yttria may be  
deposited both under and over the ceramic coat.

An improved electron beam - physical vapor deposition process is  
10 also disclosed. This method includes the step of mounting in a chamber a  
component(s) to be coated, an ingot of cubic zirconia and an ingot of  
 $Ta_2O_5$ . The two ingots being angularly spaced apart and preferably  
separated by a baffle. The ends of each of the ingots are bombarded with  
a stream of electrons to form vapors of each. The component is then  
15 alternately exposed to vapor deposition from the two vapor streams by  
rotation of the surfaces to be coated.

#### BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a cross-sectional schematic of a coated article having a  
thermal barrier coating as contemplated by the present invention.

FIG. 2 shows the effect of percent porosity<sup>5</sup> on the thermal conductivity of 7% yttria stabilized zirconia and the advantage of depositing the stabilized porosity in layers.

FIG. 3 is a schematic illustration of an apparatus suitable for  
5 carrying out a method for forming the thermal barrier coating of FIG. 1.

### DESCRIPTION OF THE PREFERRED EMBODIMENT

Referring to FIG. 1, a base metal or substrate 10 is a nickel, cobalt  
or iron based high temperature alloy from which turbine airfoils are  
commonly made. Preferably, the substrate 10 is a superalloy having  
10 hafnium and/or zirconium such as MAR-M247 and MAR-M 509, the  
compositions of which are shown in Table 1.

6  
TABLE 1

Alloy	Mo	W	Ta	Al	Ti	Cr	Co	Hf	V	Zr	C	B	Ni
Mar-M247	.65	10	3.3	5.5	1.05	8.4	10	1.4	--	.055	0.15	.15	bal.
Mar-M509	--	7.0	3.5	--	0.25	23.4	Bal.	--	--	.5	.6	--	10.0

A bond coat 12 lies over the substrate 10. The bond coat 12 is usually comprised of a MCrAlY alloy. Such alloys have a broad composition of 10 to 35% chromium, 5 to 15% aluminum, 0.01 to 1% yttrium, or hafnium, or lanthanum, with M being the balance. M is selected from a group consisting of cobalt, nickel, and mixtures thereof. Minor amounts of other elements such as Ta or Si may also be present. The MCrAlY bond coat is preferably applied by EB-PVD, through sputtering, low pressure plasma or high velocity oxy fuel spraying or entrapment plating may also be used.

Alternatively, the bond coat 12 can be comprised of an intermetallic aluminide such as nickel aluminide or platinum aluminide. The aluminide bond coat can be applied by standard commercially available aluminide processes whereby aluminum is reacted at the substrate surface to form an aluminum intermetallic compound which provides a reservoir for the growth of an alumina scale oxidation resistant layer. Thus the aluminide coating is predominately composed of aluminum intermetallic [e.g., NiAl,

7

CoAl and (Ni, Co) Al phases] formed by reacting aluminum vapor species, aluminum rich alloy powder or surface layer with the substrate elements in the outer layer of the superalloy component. This layer is typically well bonded to the substrate. Aluminizing may be accomplished by one of  
5 several conventional prior art techniques, such as, the pack cementation process, spraying, chemical vapor deposition, electrophoresis, sputtering, and appropriate diffusion heat treatments. Other beneficial elements can also be incorporated into diffusion aluminide coatings by a variety of processes. Beneficial elements include Pt, Pd, Si, Hf, Y and oxide  
10 particles, such as alumina, yttria, hafnia, for enhancement of alumina scale adhesion, Cr and Mn for hot corrosion resistance, Rh, Ta and Cb for diffusional stability and/or oxidation resistance and Ni, Co for increasing ductility or incipient melting limits.

In the specific case of platinum modified diffusion aluminide coating  
15 layers, the coating phases adjacent to the alumina scale will be platinum aluminide and/or nickel-platinum aluminide phases (on a Ni-base superalloy).

Through oxidation an alumina (i.e., aluminum oxide) layer 14 is formed over the bond coat 12. This alumina layer 14 provides both  
20 oxidation resistance and a bonding surface for a ceramic coat 16. The alumina layer may be formed before the ceramic coat 16 is applied, during application of coat 16, or subsequently by heating the coated article in an



oxygen containing atmosphere at a temperature consistent with the temperature capability of the superalloy, or by exposure to the turbine environment. The sub-micron thick alumina scale will thicken on the aluminide surface by heating the material to normal turbine exposure conditions. The thickness of the alumina scale is preferably sub-micron (up to about one micron). The alumina layer 14 may also be deposited by chemical vapor deposition or by EB-PVD following deposition of the bond coat 12.

Alternatively, the bond coat 12 may be eliminated if the substrate 10 is capable of forming a highly adherent alumina scale or layer 14. Examples of such substrates are very low sulfur (<1 ppm) single crystal superalloys, such as PWA 1487 and Rene N5, which also contain 0.1% yttrium to enhance adhesion of the thermally grown alumina scale.

The ceramic coat 16 may be any of the conventional ceramic compositions used for this purpose. A preferred composition is yttria stabilized zirconia. Alternatively, the zirconia may be stabilized with CaO, MgO, CeO<sub>2</sub> as well as Y<sub>2</sub>O<sub>3</sub>. Another ceramic believed to be useful as the columnar type coating material within the scope of the present invention is hafnia, which can be yttria-stabilized. The particular ceramic material selected should be stable in the high temperature environment of a gas turbine. The thickness of the ceramic layer may vary from 1 to 1000 microns but is typically in the 50 to 300 microns range.

The ceramic coat 16 is applied by EB-PVD and as result has a columnar grained microstructure. The columnar grains or columns 18 are oriented substantially perpendicular to the surface of the substrate 10 and extend outward from the bond coat 12. Between the individual columns 18 are micron sized intercolumnar gaps 20 that extend from the outer surface of the ceramic coat 16 to the alumina layer 14. It should be appreciated that the gaps are only illustrated in FIG. 1. The actual gaps are not necessarily bounded by straight walls as shown and need not have a constant width. In fact the gaps tend to be wider at the outer surface and narrower as the gap extends toward the alumina layer.

In a portion 26 of the grains 18 adjacent the alumina layer 14, the percentage of yttria is on the order of 6 to 8 percent with 7 percent the most preferred. The portion 26 is preferably only a few microns in thickness.

Overlying the portion 26 is a second portion 28 preferably stabilized with a percentage of yttria in the range of 6 to 25 percent. More preferably, the range is 18 to 22 percent with 20 percent the most preferred. As this portion 28 is formed by a multi-evaporation source EB-PVD process, which is described in greater detail below, nanometer size particles of second phase metal oxides such as  $Ta_2O_5$  or alumina are deposited within the columnar zirconia grains, preferably on the interfaces 22 between the sub-micron thickness layers 24 of zirconia that are deposited each time

that the component is rotated. The range of  $Ta_2O_5$  or alumina within the columnar zirconia grains is 0.5 to 15 weight percent, with a range of 1 to 4 percent preferred. The layers 24 in this portion 28 have a thickness in the range of 50 to 500 nanometers with a thickness range of 100 to 200  
5 nanometers preferred. Second phase metal oxides are oxides that do not undergo irreversible changes in composition during processing.

Overlying the portion 28 is an outer portion 30 that like portion 26 contains between 6 to 8 percent yttria with 7 percent preferred. This portion 30 is optional and increases the erosion resistance of the coating.  
10 However, neither portions 26 or 30 are essential to the practice of the present invention.

Though the Applicants do not wish to be held to a particular theory, it is believed that the second phase metal oxide nano particles essentially form stabilized porosity. The difference in thermal expansion between the  
15 metal oxide particles ( $Ta_2O_5$ ) and the ceramic (zirconia) results in a void being formed around the oxide, any sintering or chemical bonding between the zirconia and metal oxide, that occurs when the part is at temperature, is broken during subsequent cooling and reheating. While normal porosity in the zirconia would disappear as the pores sinter at the  
20 operating temperature, the presence of metal oxides stabilizes the porosity. Heat flowing through the zirconia sees the metal oxide particle as a pore. The effectiveness of second phase particle stabilized nano pores

in reducing the thermal conductivity of the zirconia was confirmed by finite element heat flow calculations. The thermal conductivity of an idealized columnar grain of zirconia as shown in Figure 1 was calculated assuming different distribution, sizes and shapes of the pores. Figure 2 compares a random distribution of spherical pores with pores randomly distributed in every fifth layer of zirconia. The pore size was  $0.01\mu\text{m}$ . The EB-PVD deposition of zirconia is in layers with every layer corresponding to one rotation of the part to be coated. The calculations also showed that for both random distributions and layered distribution the pores were more effective if they were penny shaped rather than spherical. The most effective combination being penny shaped pores randomly distributed in layers. This of course is most easily and effectively obtained by the second phase oxides being deposited between the layers of zirconia. The calculations also showed that the pore size was not critical, but preferably should be around  $0.1\mu\text{m}$ . The pore size, shape and distribution may be controlled via the evaporation and deposition conditions. For instance, increasing rotation speed will decrease layer thickness and size of the stabilized pores.

Referring to FIG. 3, an electron beam physical vapor deposition (EB-PVD) apparatus 40 generally includes a vacuum chamber 42 surrounding a component 44 mounted on a rotatable component holder 43. Two target ingots 46 and 50 are mounted in holders 47 and 51

respectively within the chamber 42. Ingot 46 is preferably zirconia and ingot 50 is preferably  $Ta_2O_5$  or alternatively  $Al_2O_3$ . The ingots 46 and 50 are preferably between 45 to 180 degrees apart with 90 degrees preferred. A baffle 60 may be disposed between the ingots to prevent the evaporation spray or vapor 48 from one to interfere with the evaporation spray or vapor 52 of the other. Two electron beam guns 54,56 are employed with one directed to the ingot 46 and the other to the ingot 50. In use the chamber 42 is evacuated by pumps (not shown). As the mounted components are rotated, the guns 54, 56 supply a stream 58 of high energy electrons to the surface of the ingots respectively. The ingots evaporate causing zirconia vapors and  $Ta_2O_5$  vapors that subsequently condense onto the rotating component. Thus, as the component rotates first a layer of zirconia is deposited than a layer of  $Ta_2O_5$  is deposited, then another layer of zirconia, etc. This process continues until a preselected thickness of the ceramic coat on the component is obtained. To insure that the deposited vapors are fully oxidized and oxygen rich gas is usually supplied into the chamber 42 through a tube not shown. Because the percent of second phase oxide addition to the zirconia is small it is possible to use ingots of the pure metal, rather than the oxide and allow the oxide to form in the vapor cloud. this preferably requires a small increase in oxygen flow rates above that used to ensure that the zirconia is fully oxidized.

Various modifications and alterations to the above-described preferred embodiment will be apparent to those skilled in the art. Accordingly, this description of the invention should be considered exemplary and not as limiting the scope and spirit of the invention as set forth in the following claims.

**What is Claimed is:**

1. A superalloy article having a ceramic thermal barrier coating on at least a portion of its surface comprising a superalloy substrate (10), a bond coat (12) overlying the substrate (10) and selected from the group  
5 consisting of aluminides and MCrAlY where M is a metal selected from the group consisting of iron, cobalt, nickel, and mixtures thereof, and a columnar grained ceramic coat (16) over said bond coat (12), the columnar grained ceramic coat (16) characterized by having a first portion (28) formed of a plurality of layers (24) of zirconia stabilized with 20  
10 percent yttria and having interfaces (22) between the layers (24) decorated with particles selected from a group consisting of Ta<sub>2</sub>O<sub>5</sub> and alumina.
2. The article of claim 1 wherein said ceramic coat (16) further comprises a layer (26) of zirconia is stabilized with 6 to 8 percent yttria  
15 between said bond coat (12) and said first portion (28).
3. The article of claim 2 wherein said layer (26) of zirconia is stabilized with 7 percent yttria.
4. The article of claim 2 further comprising a second layer (30) of zirconia stabilized with 6 to 8 percent yttria over said first portion (28).
- 20 5. The article of claim 4 wherein said second layer (30) of zirconia is stabilized with 7 percent yttria.

6. The article of claim 4 wherein said second layer (30) of zirconia has an electrically biased outer surface (32).

7. The article of claim 1 further comprising an oxidation resistant layer (14) between said bond coat (12) and said columnar  
s grained ceramic coat (16).

8. The article of claim 7 wherein said oxidation resistant layer (14) is alumina.

9. The article of claim 7 wherein said oxidation resistant layer (14) is an alumina scale.



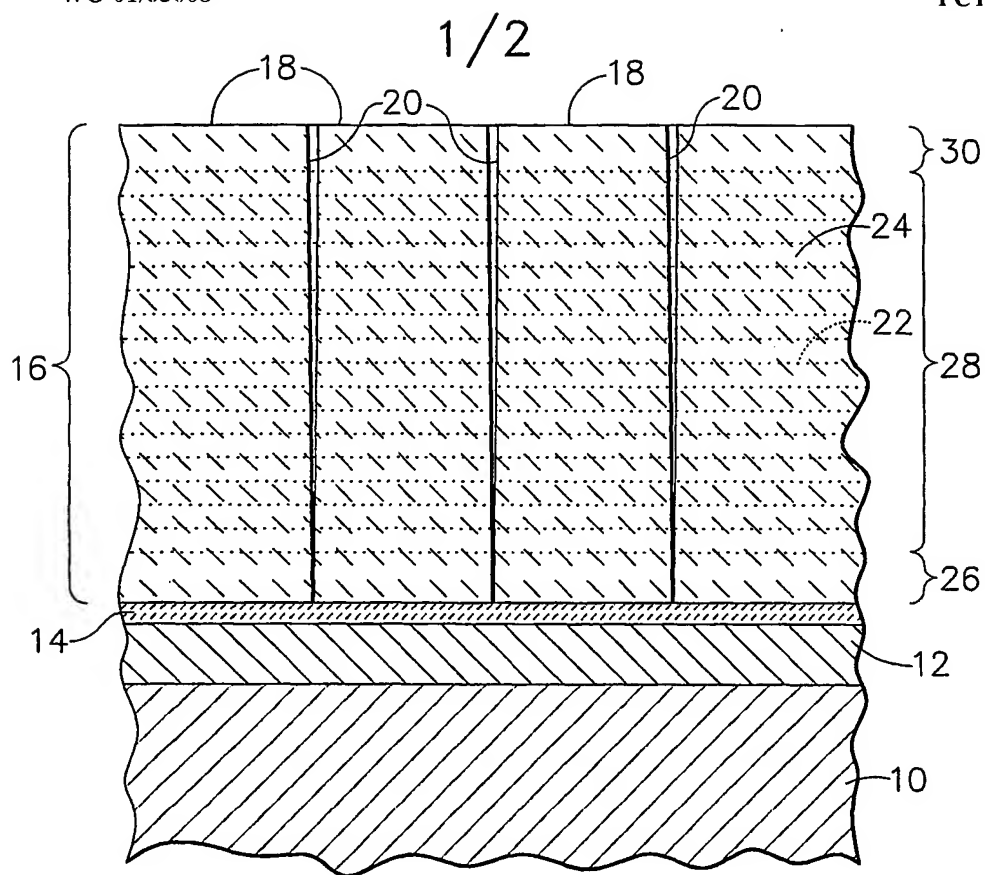


FIG. 1

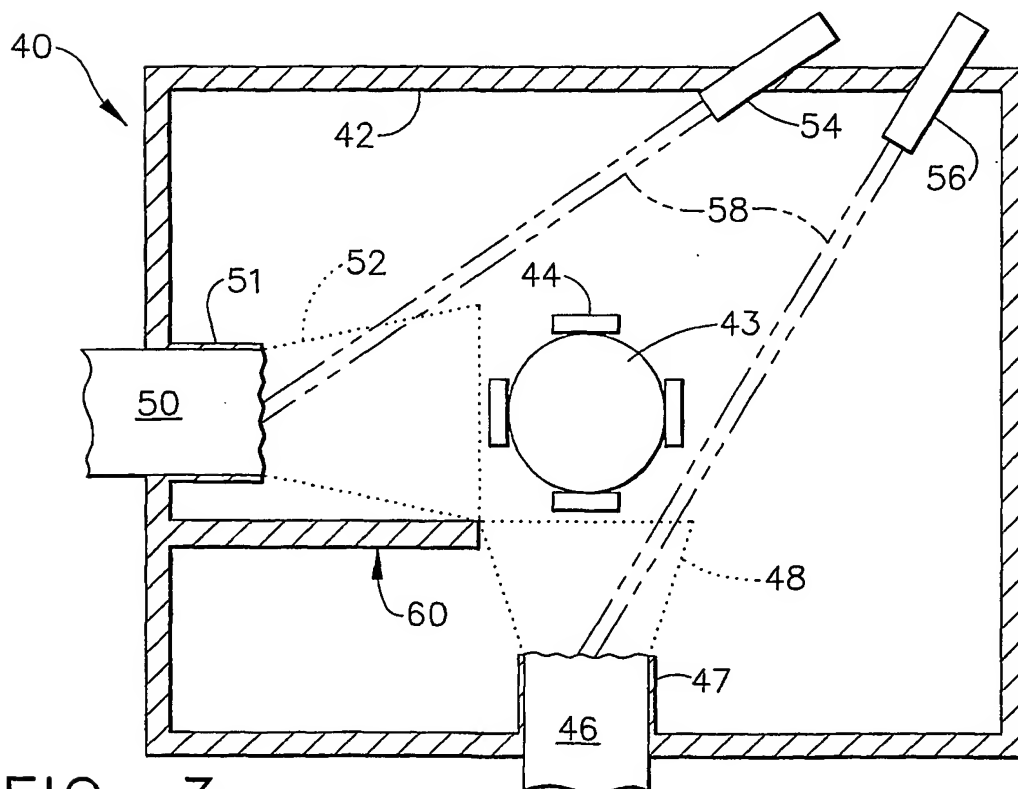


FIG. 3

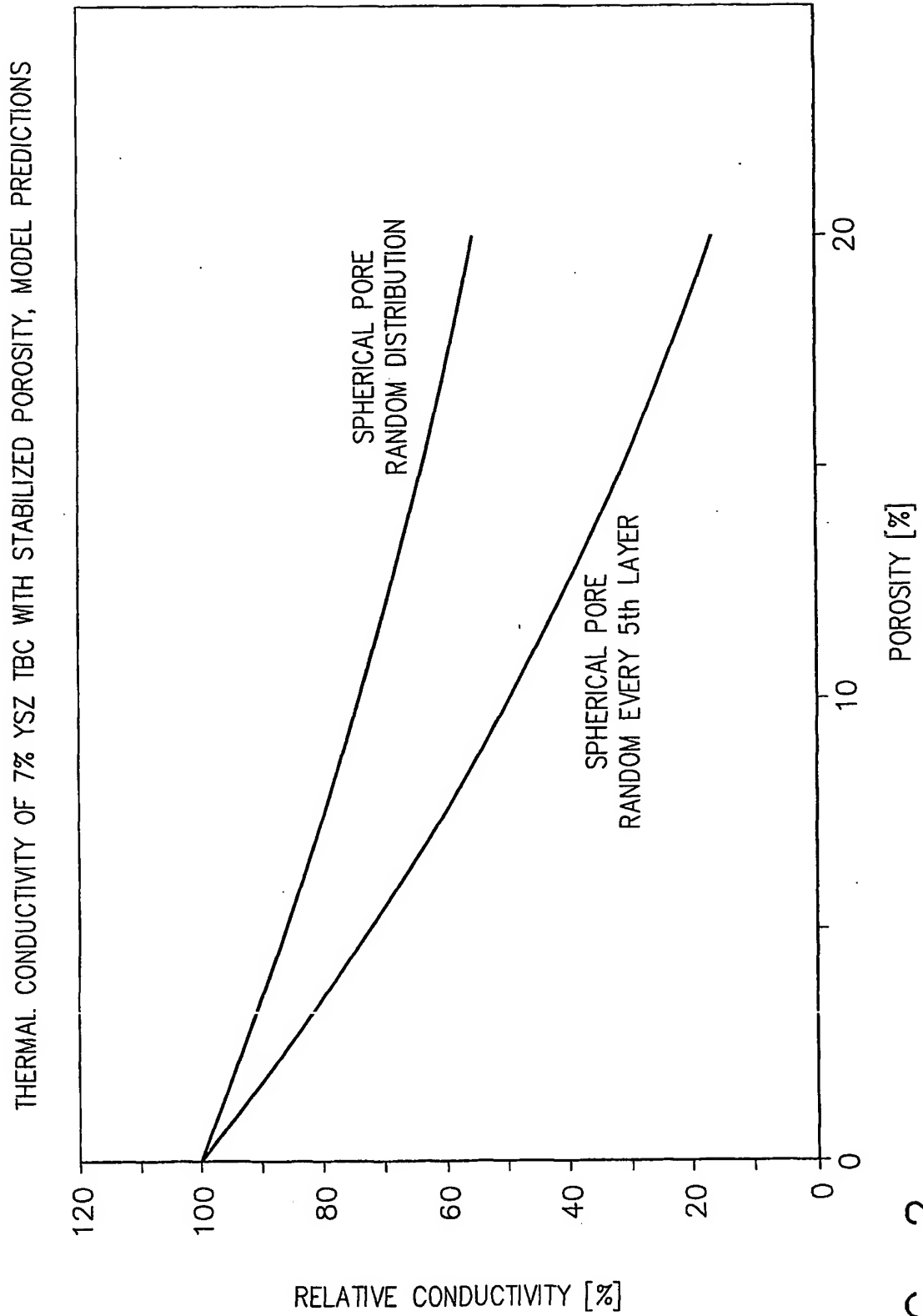


FIG. 2

(19) World Intellectual Property Organization  
International Bureau



(43) International Publication Date  
30 August 2001 (30.08.2001)

PCT

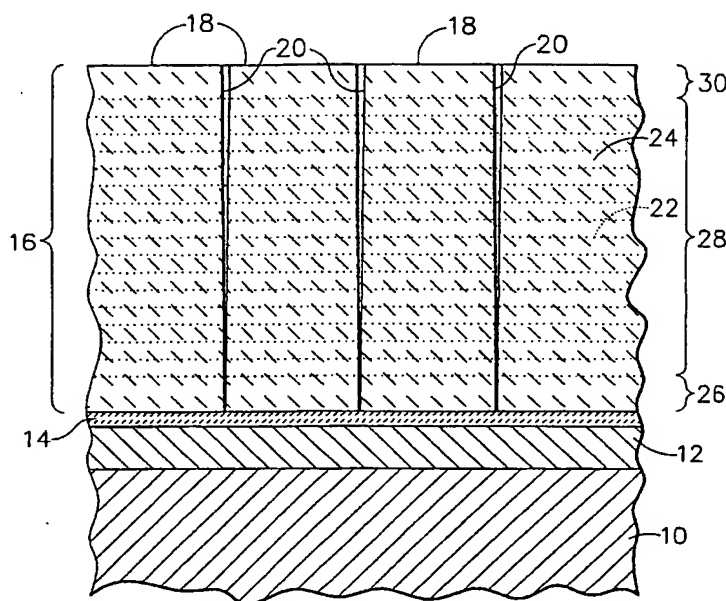
(10) International Publication Number  
**WO 01/63008 A3**

- (51) International Patent Classification<sup>7</sup>: C23C 28/00 (74) Agents: CRISS, Roger, H. et al.: Honeywell International Inc., 101 Columbia Avenue, P.O. Box 2245, Morristown, NJ 07962-2245 (US).
- (21) International Application Number: PCT/US01/09266
- (22) International Filing Date: 22 March 2001 (22.03.2001) (81) Designated State (national): JP.
- (25) Filing Language: English (84) Designated States (regional): European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR).
- (26) Publication Language: English
- (30) Priority Data: 09/535,394 24 March 2000 (24.03.2000) US Published:  
— with international search report  
— upon request of the applicant, before the expiration of the time limit referred to in Article 21(2)(a)
- (71) Applicant: HONEYWELL INTERNATIONAL INC.  
[US/US]: 101 Columbia Avenue, P.O. Box 2245, Morristown, NJ 07960 (US). (88) Date of publication of the international search report:  
28 February 2002

(72) Inventors: STRANGMAN, Thomas, E.; 7632 North 22nd Street, Phoenix, AZ 85020 (US). RAYBOULD, Derek; 2 Horizon Drive, Denville, NJ 07834 (US).

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: LOWER CONDUCTIVITY THERMAL BARRIER COATING



(57) Abstract: A thermal barrier coating for superalloy articles such as turbine engine vanes and blades that are exposed to high temperature gas is disclosed. The coating includes a columnar grained ceramic layer applied to an aluminide or MCrAlY bond coat by electron beam physical vapor deposition. The ceramic layer is comprised a plurality of layers of zirconia stabilized with 20 percent yttria and the interfaces between the layers are decorated with particles selected from a group consisting of Ta<sub>2</sub>O<sub>5</sub> and alumina. Though not essential to the invention a layer of tetragonal zirconia may be deposited both under and over the ceramic coat. An improved electron physical beam vapor deposition process for applying this ceramic layer is also disclosed.

WO 01/63008 A3

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 7 C23C28/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
IPC 7 C23C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, COMPENDEX

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 059 095 A (KUSHNER BURTON A ET AL) 22 October 1991 (1991-10-22) column 2, line 29 - line 53 column 3, line 15 - line 62 claims 1-9,11,12,15; example 5 ---	1,7,9
P,X	WO 01 18274 A (SIEMENS WESTINGHOUSE POWER) 15 March 2001 (2001-03-15) page 3, paragraph 2 -page 4, paragraph 2 page 5, paragraph 3 page 6, paragraph 2 -page 8, paragraph 2 page 9, paragraph 3 - paragraph 4 ---	1,7,9
A	EP 0 783 043 A (GEN ELECTRIC) 9 July 1997 (1997-07-09) the whole document --- -/--	1,7-9

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

\* Special categories of cited documents :

- \*A\* document defining the general state of the art which is not considered to be of particular relevance
- \*E\* earlier document but published on or after the international filing date
- \*L\* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- \*O\* document referring to an oral disclosure, use, exhibition or other means
- \*P\* document published prior to the international filing date but later than the priority date claimed

- \*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- \*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- \*Y\* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- \*G\* document member of the same patent family

Date of the actual completion of the international search

29 October 2001

Date of mailing of the international search report

06/11/2001

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl.  
Fax: (+31-70) 340-3016

Authorized officer

Ceulemans, J

## INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 01/09266

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5 906 895 A (TAKAHASHI MASASHI ET AL) 25 May 1999 (1999-05-25) the whole document ---	1
A	US 4 916 022 A (SOLFEST PATRICIA A ET AL) 10 April 1990 (1990-04-10) the whole document ---	1-9
E	DE 100 08 861 A (KERNFORSCHUNGSANLAGE JUELICH) 6 September 2001 (2001-09-06) the whole document -----	1-5

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 01/09266

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 5059095	A	22-10-1991	NONE	
WO 0118274	A	15-03-2001	US 6294260 B1 WO 0118274 A1	25-09-2001 15-03-2001
EP 0783043	A	09-07-1997	US 5683825 A DE 69607449 D1 DE 69607449 T2 EP 0783043 A1 JP 9279364 A	04-11-1997 04-05-2000 26-10-2000 09-07-1997 28-10-1997
US 5906895	A	25-05-1999	JP 10088368 A CN 1178204 A , B DE 19741223 A1 GB 2317400 A , B	07-04-1998 08-04-1998 02-04-1998 25-03-1998
US 4916022	A	10-04-1990	NONE	
DE 10008861	A	06-09-2001	DE 10008861 A1 WO 0163006 A1	06-09-2001 30-08-2001

Form PCT/ISA/210 (patent family annex) (July 1992)